

Initial Tests to Characterize Block Copolymer Self-assembled Nanostructures with NEXAFS Microscopy

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INTRODUCTION

Block copolymers (BCP) are fascinating materials that can form a variety of self-assembled structures. Diblock copolymers, for example, form lamella, cylinders, spheres, as well as more complicated structures, depending on the relative length and incompatibility of the blocks. More complex and a larger number of structures are formed by triblock BCPs and related multifunctional materials. BCP have a great potential to be used as templating materials for various nano-structures, and have been used for example to create vertical arrays of nanowires with densities in excess of 1.9×10^{11} wires per square centimeter [1]. More complicated multicomponent systems that involve mixtures and blends of homopolymers and block copolymers might also exhibit interesting fundamental properties that need to be researched and that could be exploited for patterning. Generally, diblock copolymers are easily characterized with conventional tools such as Atomic Force Microscopy (AMF) and Transmission Electron Microscopy (TEM). However, characterization of more complex multicomponent systems requires the distinction of more than two polymeric species, a challenge that can lead to ambiguities with conventional characterization tools. Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) microscopy has the capability to distinguish a variety of polymer species [2,3] and might thus be an excellent tool to characterize complex system containing blockcopolymers. For example, NEXAFS microscopy should be able to characterize the location and centralization of a functionally unique homopolymer in multiblock copolymer self-assembled nanostructure. In order to test the ability of NEXAFS microscopy to image the nanostructures formed by relatively low molecular weight block copolymers we characterized various poly(styrene-*b*-ethylene oxide), p(S-*b*-EO), thin films that exhibited a cylindrical morphology.

EXPERIMENTAL

Nominally 200 nm thick films of p(S-*b*-EO) were spun cast or solution cast and solvent-vapor annealed at room temperature. The samples were transferred to TEM grids for investigation with the 5.3.2 Polymer STXM [4]. Photon energies near the carbon K absorption edge were used to image the morphology and to assess the film thickness variations. An energy of 285.15 eV provides particularly good contrast between PS and PEO. At this energy, the PS block is highly absorbing whereas the PEO block has little absorbance. The p(S-*b*-EO) BCP used were 70% PS and had total molecular weight of 25,000 g/mol and 90,000 g/mol. These sample compositions and the preparation conditions chosen resulted in PEO cylinders in a PS matrix, with the PEO cylinders aligned along the substrate normal.

RESULTS AND DISCUSSION

A total of 8 different samples were imaged at a number of photon energies to explore the relative contrast obtainable in these materials. We show as an example images at 285.1 eV of the 90k p(S-*b*-EO) sample in Fig. 1. Cylindrical EO microdomains about 50 nm in size, or about 100 nm spaced, are arranged in a near hexagonal pattern and clearly visible. In addition, larger “features” can be seen in the micrographs. Images at other photon energies confirm that these features are thickness variations of the films.

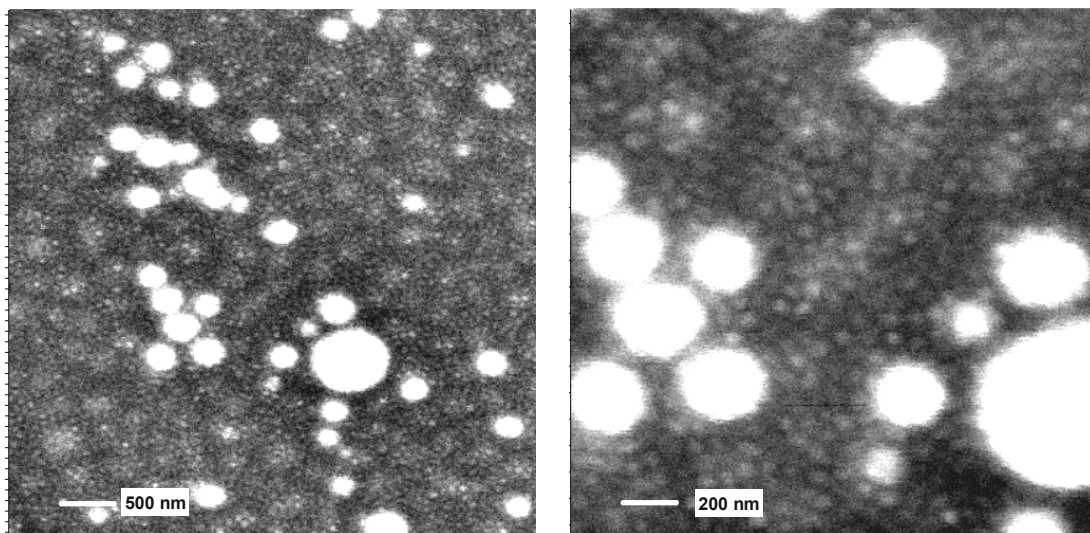


Fig. 1. STXM images at 285.1 eV of 90k-p(S-*b*-EO) at two different magnifications. Besides the near hexagonally arranged EO cylindrical microdomains of about 50 nm in size, larger features that are film thickness variations are visible.

Images of the 25k- p(S-*b*-EO) exhibited similar hexagonal patterns. Due to the lower molecular weight, these features are smaller and are near the visibility limit of the microscope of 30 nm. Similar thickness variations to those observed in the 90k p(S-*b*-EO) samples were also observed in the 25k- p(S-*b*-EO) samples.

The thickness variation in these samples indicates that this particular batch of samples might have not been optimally processed and/or completely phase separated. In general, the sample preparation of these materials is very sensitive on the environmental conditions, such as humidity. Nonetheless, the results indicate that NEXAFS microscopy can image the self-assembled microstructure in real, low molecular weight BCP samples with very small structures.

CONCLUSION

We have successfully imaged the microstructure of model block copolymer self-assemblies. Our results show that NEXAFS microscopy should have the required spatial resolution to successfully characterize complex polymeric mixture and materials that contain BCPs.

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